PB86-118825

Fuel Oil Reburning Application for NOx Control to Firetube Package Boilers

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-118825

EPA/600/D-85/262
October 1985

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J. A. Mulholland
and
R. E. Hall

U. S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/D-85/262	2.	3. RECIPIENT'S ACCESSION NO. PB86 118257/AS
4. TITLE AND SUBTITLE Fuel Oil Reburning Application for NO_x Control to Firetube Package Boilers		5. REPORT DATE October 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) James A. Mulholland and Robert E. Hall		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS See Block 12.		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-3988
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development, Air and Energy Engineering Research Laboratory, Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES AEERL project officer is J. A. Mulholland, Mail Drop 65, 919/514-7663.		

16. ABSTRACT The paper discusses retrofitting two 1.0 MW (3.5 million Btu/hr) firetube package boilers for fuel oil reburning application for NOx emission control. An overall NOx reduction of 46% from an uncontrolled emission of 125 ppm (dry, at 0% O2) was realized by diverting 20% of the total boiler load to a distillate-fuel-oil-fired second stage burner; a 51% NOx reduction from 265 ppm was achieved in a distillate/residual fuel oil mixture (0.14% nitrogen content) reburning application. Nitrogen-free fuel oil reburning was found to be slightly more effective at reducing NOx than natural gas reburning, although longer fuel-rich zone residence times were required to allow for evaporation and mixing of the fuel oil droplets. The key parameters investigated, that impact the reburning process, were: primary flame NOx, reburn zone stoichiometry, and reburn zone residence time. Reburning applied to firetube package boilers requires minimal facility modification. Reburning can be coupled with other NCx control techniques (e.g., distributed-air low NCx burners) to achieve NOx emissions of less than 100 ppm; however, for very low primary flame NOx conditions (i.e., < 200 ppm), reburning fuel nitrogen content is a limiting factor, and reburning with a low nitrogen content fuel must be considered.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Nitrogen Oxides	Stationary Sources	07B
Fuel Oil	Reburning	21D
Combustion	Staged Fuel Combustion	21B
Firetube Boilers		13A
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 30
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

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By:

J. A. Mulholland
and
R. E. Hall
U. S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

ABSTRACT

Two pilot-scale (0.73 MW) firetube package boilers were retrofitted for fuel oil reburning application for NO_x emission control. When firing distillate fuel oil (0.01 percent nitrogen content), an overall NO_x reduction of 46 percent from an uncontrolled emission of 125 ppm (dry, at zero percent O_2) was realized by diverting 20 percent of the total boiler load to a second stage burner; a 51 percent NO_x reduction from 265 ppm was achieved in a distillate/residual fuel oil mixture (0.14 percent nitrogen content) reburning application. Nitrogen-free fuel oil reburning was found to be slightly more effective at reducing NO_x than was natural gas reburning, though longer fuel-rich zone residence times were required to allow for evaporation and mixing of the fuel oil droplets. Key parameters investigated which impact the reburning process were: primary flame NO_x, reburn zone stoichiometry, and reburn zone residence time.

Reburning applied to firetube package boilers requires minimal facility modification. Reburning can be coupled with other NO_x control techniques (e.g., distributed air low NO_x burners) to achieve NO_x emissions of less than 100 ppm. However, for very low primary flame NO_x conditions (i.e., less than 200 ppm), reburning fuel nitrogen content is a limiting factor, and reburning with a low nitrogen content fuel, such as natural gas or nitrogen-free distillate oil, may be necessary to achieve 50 percent NO_x reduction.

INTRODUCTION

Oxides of nitrogen (NO_x) are formed during combustion by the reduction and oxidation of molecular nitrogen and nitrogen contained in the fuel. Because NO_x emitted from stationary combustion sources contributes to the degradation of air quality as well as to acid deposition and forest damage, various control technologies have been developed to reduce emissions. Many of the NO_x control technologies currently in use involve modification of the combustion process to reduce peak flame temperatures and create fuel-rich conditions by altering fuel and oxidizer mixing rates. Thus, NO_x formation, a kinetically controlled process, is minimized. However, NO_x control can also be achieved by removing NO_x from the combustion products after they are formed. Reburning, or fuel staging, is an in-furnace NO_x control strategy that accomplishes this.

As many as 30 years ago (1,2), experimental results were available indicating that NO_x could be destroyed by reaction with hydrocarbon radicals. Commercial utilization of this reaction mechanism occurred in the late 1960's by the John Zink Corporation who patented an NO_x control process for nitric acid plants (3) based on staged injection of natural gas. Early fundamental studies of NO_x

destruction by injection of secondary fuel into the flame zone were performed by Wendt et al. (4), who coined the name "reburning" to describe the process. Concerted effort to develop reburning for application to boilers occurred in Japan during the late 1970's and early 1980's. The first reporting of these efforts was by Takahashi et al. (5), documenting extensive laboratory-, pilot-, and full-scale evaluation of a fuel staging process they refer to as Mitsubishi Advanced Control Technology, or MACT. MACT results indicate that NO_x emissions can be reduced by at least 50 percent independent of initial NO_x level and fuel type. These promising results have renewed interest in reburning, and further development is being sponsored by the U. S. Environmental Protection Agency (EPA), the Electric Power Research Institute, the Gas Research Institute, and the U. S. Department of Energy.

Application of reburning involves diverting portions of the fuel and combustion air streams from the main burner(s) for injection into the post-flame gases. Thus, reburning establishes a three-stage combustion process, consisting of a fuel-lean primary zone, a fuel-rich reburning zone, and a fuel-lean burnout zone. NO_x reduction via reburning occurs in two ways: NO_x formation is inhibited due to reduced mixing intensities in the derated primary burner zone and fuel-rich conditions in the secondary combustion zone, and NO_x destruction is promoted due to secondary flame radical attack on nitric oxide (NO) produced in the primary zone to form molecular nitrogen (N_2). Maximizing the destruction component of NO_x reduction is a key to optimizing the reburn technology. Bench-scale tests (6,7) have been used to verify the hypothesized NO_x destruction mechanism, represented in a simple form as follows:

$$NO \xrightarrow{CH} HCN \xrightarrow{OH,\ H} NH \begin{cases} \xrightarrow{OH,H} NO \\ \xrightarrow{NO} N_2 \end{cases} . \qquad (1)$$

Commercial utilization of reburning has been achieved in Japan, where NO_x emission regulations are stringent, by Hitachi Zosen (8) and Ishikawajima-Harima Heavy Industries (9), as well as Mitsubishi Heavy Industries (10). In the U. S., bench- and pilot-scale evaluation of gas, oil, and coal reburning processes continues (11,12,13). Application of reburning to a coal-fired industrial boiler, sponsored by the U. S. Environmental Protection Agency (EPA), is scheduled to begin in 1986. While relatively inexpensive distributed air low-NO_x burner designs have been developed to meet current federal and state NO_x emission standards (in the 300 to 500 ppm range), reburning offers a means to reduce NO_x emissions by another 50 percent without impacting furnace combustion efficiency.

The current study utilizes two pilot-scale firetube package boiler test facilities located in EPA's Environmental Research Center in Research Triangle Park, North Carolina. Tests were performed to evaluate fuel oil reburning application at low primary combustion NO_x levels (50 to 250 ppm, measured dry and corrected to zero percent O_2)[1] and low reburn zone temperatures (1300 to 1600 K). An NO_x emission level of approximately 200 ppm represents the minimum level attainable

[1] All NO_x concentrations are reported on a dry basis, and corrected to zero percent O_2, in this paper.

by practical in-furnace NO_x control technologies currently in use. The relatively low radiant zone temperatures are characteristic of small commercial firetube package boilers. Previously documented tests on these facilities have shown that natural gas reburning effectiveness in NO_x control decreases as primary NO_x levels decrease (14,15). That is, NO_x reduction via natural gas reburning is not first order with respect to primary NO_x. It has also been shown that, at low initial NO_x levels, volatile nitrogen in the reburning fuel limits reburning effectiveness (16). This paper describes tests to firetube package boilers that evaluate these results for fuel oil reburning application.

EXPERIMENT

Apparatus

Two pilot-scale firetube package boiler test facilities, each rated at 0.73 MW (2.5×10^6 Btu/hr) heat input and capable of firing gaseous and liquid fuels, were modified to accommodate fuel oil reburning for this series of experiments. A package boiler simulator (PBS) fitted with a low NO_x precombustion chamber burner, shown in Figure 1a, was utilized to perform parametric input/output and detailed tests to evaluate fuel oil reburning effectiveness. A North American Scotch-type package boiler, shown in Figure 1b, was used to verify PBS test results and demonstrate optimized fuel oil reburning application.

The radiant section of the PBS is cooled with Dowtherm G®, with absorbed heat dumped to atmosphere via a cooling tower. The horizontal radiant section is 0.6 m (2 ft) in diameter and 3.0 m (10 ft) in length. Combustion gas exits the boiler through a vertical stack. A commercial burner originally installed on the research boiler was replaced with a low NO_x precombustion chamber burner patterned after the unit developed by England *et al.* (17). This major facility modification was made to achieve control of the NO_x concentration at the plane of secondary fuel injection, independent of boiler fluid mechanics. The prechamber itself is a refractory tunnel designed for near adiabatic conditions and contains a fuel-rich flame. At the interface between the prechamber and the radiant section, the flow path is constricted through a 25 cm (10 in.) diameter throat. Eight ports, located in this throat region, allow staged combustion air to be injected radially inward. This air mixes rapidly with the fuel-rich exhaust from the prechamber and produces a fuel-lean, essentially premixed flame in the radiant section. Multiple ports allow for radial and axial insertion of various sample probes and staged fuel and air injectors.

Reburning fuel oil was injected through a heat-traced line contained in a water-cooled, stainless steel jacket inserted through a side port in the PBS. A 45-degree hollow-cone fuel spray was achieved with a pressure-atomizing nozzle directed downstream into the primary combustion exhaust along the boiler centerline. Final burnout air was injected downstream of the staged fuel injection location through eight radial ports in a water-cooled boom inserted down the boiler centerline through a rear flange.

The North American boiler is a three-pass unit, 0.6 m (2 ft) in internal diameter and 3.0 m (10 ft) in length, with a continuous service rating of 1089 kg (2400 lb) of steam per hour. The mechanical linkage for automatic control of air/fuel ratio with load variation was disconnected from the burner and replaced with a manual adjustment that permits independent control of primary flame excess air at any desired load.

Reburning fuel and final burnout air were injected down the centerline of the North American boiler through a water-cooled boom assembly inserted through a modified maintenance access plate at the rear of the boiler. The assembly consists of two concentric telescoping injectors, with the inner injector supplying reburning fuel through a heat-traced line and the outer injector providing burnout air in eight radial jets. As in the PBS, a 45-degree hollow-cone, pressure-atomized fuel spray was produced, but, here, was directed upstream into the primary combustion gas.

The experimental facilities were designed with independent control of each fuel, fuel dopant, and air stream. Natural gas, distillate fuel oil, and a distillate/residual fuel oil mixture were fired, with ammonia and pyridine dopants being used to simulate fuel-bound nitrogen. Ammonia was injected into the natural gas delivery system sufficiently upstream to ensure thorough mixing before entry to the combustion system. Distillate fuel oil, containing 0.01 percent (by weight) nitrogen, was doped with pyridine to achieve a 0.5 percent fuel nitrogen batch mixture. The distillate/residual fuel oil mixture contains 0.14 percent nitrogen. This heavier fuel oil, with a net viscosity of a light No. 5 fuel oil, was preheated to 370 K (200°F) prior to injection. A comparison of various properties of these fuels is presented in Table 1.

Methods

All gas flows were measured independently using various types of head meters. The fuel oil volumetric flow rate was measured with a calibrated metering pump.

Stack and in-flame combustion gas speciation, temperature, and velocity were measured. A sampling panel board provided for continuous measurement of NO_x, CO, CO_2, THC, and O_2 concentrations, as defined in Table 2. In-flame species concentrations were determined by extracting samples through a water-cooled stainless steel probe and ducting the sample gases to the continuous emission monitors. The sample probe is equipped with a water quench spray which was activated during batch sampling to collect HCN and NH_3 in solution from the reacting gas. HCN and NH_3 concentrations were measured using specific ion electrode techniques. The collection efficiency for HCN was experimentally determined to be 70 percent. Ammonia collection efficiency was found to be nearly 100 percent. Nitrous oxide (N_2O) was measured with a gas chromatograph equipped with an electron capture detector and a 3.66 m (12 ft) long stainless steel column packed with Porapak Q®.

Flame temperature measurements utilize suction pyrometers equipped with R-type (platinum-platinum/13% rhodium) thermocouples. A short pyrometer was inserted through sidewall ports in the furnace to measure radial temperature profiles. A long pyrometer was used to measure axial temperature profiles through the entire length of the radiant section at three different radii.

Velocity profiles at the secondary fuel injection plane are derived from measurements made with a Prandtl probe inserted through a port in the boiler sidewall. Measurement of the dynamic pressure differential in the radiant section of a firetube package boiler was particularly difficult due to the low mean velocity (less than 5.0 m/sec) and the high apparent turbulent fluctuations. Pressures from 0.1 to 100 Pa (0.001 to 1 torr) were measured using a differential pressure transducer in tandem with an electronic manometer (Barocell model 1173),

providing a 0 to 1 V linearized electrical output. To determine the average square root of the pressure differential, the electrical output was sampled by a microcomputer at an approximate rate of 15 Hz with the square root of approximately 1250 individual readings taken at each point. With this technique it is possible to obtain accurate measurements (with mean and standard deviation repeatable to at least two significant digits) for boiler radiant section velocities greater than 3.0 m/sec (10 ft/sec). It is significant to note that the ratio of the standard deviation to the mean was often in excess of 50 percent, increasing with decreasing velocity.

Approach

This paper, describing a series of pilot-scale experiments designed to investigate fuel oil reburning application for in-furnace NO_x control, provides information bridging the gap between fundamental studies of NO/hydrocarbon reaction mechanisms and full-scale field applications of reburning. The firetube package boilers used in this study have single centerline burners and relatively simple furnace geometries (right circular cylinders), allowing for complete spatial and temporal characterization of experimental conditions while providing thermal and fluid mechanical environments typical of small commercial systems.

Three objectives were defined at the outset of the experimental program. First, parametric tests were performed in the PBS to characterize the fuel oil reburning process at a practical level. Key process parameters to be varied independently were identified, as listed in Table 3. In this paper, light and heavy fuel oil reburning test results are discussed which describe the effects of three of these parameters: primary NO_x concentration, reburn zone stoichiometry, and reburn zone residence time. Separate papers have been published, or are in preparation or review, on natural gas reburning application (14), reburning fuel mixing rate effects (in review), reburn zone thermal environment effects (in preparation), and reburning fuel nitrogen content effects (16). A second objective of this study was to evaluate the validity of proposed reburning reaction mechanism by making detailed measurements of intermediate nitrogenous species in the reburn zone of the PBS. Third, fuel oil reburning application was to be optimized in the North American boiler.

RESULTS

Parametric tests, in-flame measurement tests, and optimization tests are discussed.

Parametric Tests

In the PBS tests, primary burner load was held constant at 0.59 MW (2.0×10^6 Btu/hr). A precombustion chamber stoichiometry of 0.61 was maintained to allow for primary NO_x variation from 50 to 250 ppm, adjusted by varying the amount of ammonia injected into the primary natural gas stream up to 0.75 percent. A secondary combustion air addition rate was established such that a primary zone excess air level of 5 to 10 percent was achieved. Under these conditions, the primary flame extended approximately 0.9 m (35 in.) into the boiler. At the 1.02 m (40 in.) axial location, the radial profile of O_2 concentration was essentially flat. Also, this location was just downstream of the point at which flow from the precombustion chamber constriction reattached to the boiler wall. Thus, a nominal

location for secondary fuel injection of 1.02 m (40 in.) was chosen. Final burnout air was staged at 1.63 m (64 in.), providing a 200 millisecond reburn zone bulk residence time. For natural gas reburning, this reburn zone length was found to be the minimum necessary to achieve maximum NO_x reduction.

The temperature and velocity profiles measured at the location of reburn fuel injection are shown in Figure 2. Temperatures ranged from 1200 K (1700°F) near the wall to 1600 K (2420°F) at the boiler centerline. These low radiant zone temperatures are characteristic of small package boilers. It was found that this was the low temperature limit at which the fuel oil could be injected without heavy sooting in the reducing zone. The combustion gas flow is not plugged, with a peak velocity of over 15 m/sec (50 ft/sec) and a mean velocity of 3 m/sec (10 ft/sec).

Input/output fuel oil reburning trials were performed at three levels of primary zone NO (NO_{PRI}) and three reburn zone stoichiometries (SR_R). Results from these tests using distillate oil and distillate/residual oil mixture as reburning fuels are shown in Figures 3 and 4, respectively. In these figures the abscissa is SR_R, varied by adjusting the flow rate of reburning fuel, and the ordinate is the percent ratio of exhaust NO (NO_{EX}) to NO_{PRI}. Thus, the ordinate is equivalent to 100 percent minus the percent NO reduction via reburning. Each curve represents a line of constant NO_{PRI}. These results show clearly that NO_x control by reburning is a function of primary zone NO_x, reburn zone stoichiometry, and reburning fuel properties.

To show the dependence of NO_x reduction on NO_{PRI}, the light and heavy fuel oil reburning data are replotted in Figure 5 for a reburn stoichiometry of 0.90. The overall rate of change of NO in the reburning process can be expressed as:

$$\frac{d[NO]}{dt} = -k_1 [NO]^a + k_2 \qquad (2)$$

where k_1 is an overall destruction rate term, "a" is the overall order of destruction with respect to NO, and k_2 is a formation term which is assumed in this expresion to be independent of NO concentration.[1]. Equation 2 is evaluated for two limiting cases. First, if k_2 is small relative to the k_1 term, as would be the case for high initial NO_x, the equation can be integrated to yield:

$$\frac{NO_{PRI}}{NO_{EX}} = \left[1 - (a-1)k_1 t\, NO_{PRI}^{(a-1)}\right]^{1/(a-1)}, \quad a>1. \qquad (3)$$

---

1 The formation of NO in the reburning zone, via either the Fenimore "prompt" NO mechanism or fuel-bound nitrogen oxidation (reburn zone temperatures are too low to result in NO formation by the Zeldovich "thermal" NO mechanism), is not independent of NO_{PRI}. It has been shown that, for NO_{PRI} less than 250 ppm, SR_R between 0.75 and 1.0, and volatile fuel nitrogen content of up to 1 percent, reburning fuel nitrogen to exhaust NO net conversion is 30 to 40 percent (16). Reburning prompt NO formation was found to range from 20 to 30 ppm. Therefore, over the range of NO_{PRI} considered in this paper, the assumption that reburning NO formation is independent of NO_{PRI} is approximately true. It should also be noted that, at high NO_{PRI} conditions, fuel nitrogen may result in a net increase in NO reduction due to amines formed from the fuel nitrogen reacting with NO to form N_2. It has been shown by, as yet, unpublished data that, for high NO_{PRI} conditions (greater than 500 ppm), reburn zone ammonia injection increases reburning NO_x reductions.

Here, as NO_{PRI} approaches zero, NO_{PRI}/NO_{EX} approaches 1. Using this expression, a curve fit to the natural gas reburning data is shown in Figure 5. The natural gas data are consistent with an overall order of NO destruction of 1.5 with respect to NO_{PRI}, with the formation term being negligible for NO_{PRI} greater than 50 ppm. Therefore, the first order reductions ("a" = 1) achieved by the MACT researchers (5) must be due to NO_x control techniques applied in addition to reburning, such as flue gas recirculation and selective catalytic reduction.

At low NO_{PRI} conditions, where the NO formation term dominates the NO destruction term of equation 2 (i.e., $k_2 >> k_1 [NO]^a$), integration yields:

$$\frac{NO_{PRI}}{NO_{EX}} = \left(1 + \frac{k_2 t}{NO_{PRI}}\right)^{-1} \qquad (4)$$

In this equation, as NO_{PRI} approaches zero, NO_{PRI}/NO_{EX} approaches zero; for large NO_{PRI}, NO_{PRI}/NO_{EX} approaches one. A curve representing equation 4 is also shown in Figure 5.

The fuel oil reburning data plotted in Figure 5 lie between the two limiting curves. For low NO_{PRI} conditions, the NO formation term is significant. At high NO_{PRI} conditions, the data appear to be approaching the natural gas results described by the destruction term curve with an order of 1.5 with respect to NO_{PRI}. Thus, it is shown that, as initial NO_x is decreased, it becomes more difficult to reduce NO_x via reburning, and fuel nitrogen can limit reburning effectiveness.

There exists an optimum reburn zone stoichiometry for maximum NO_x reduction by reburning. This optimum is a function of NO_{PRI} and reburning fuel nitrogen content. Figures 3 and 4 show that, for high levels of NO_{PRI} (greater than 200 ppm), maximum NO_x reductions are achieved for reburn zone stoichiometries less than 0.85 (reburn load/primary load greater than 25 percent). As the NO_{PRI} level decreases, the optimum SR_R increases. For the distillate/residual fuel oil mixture containing 0.14 percent nitrogen, at an initial NO level of 82 ppm, the minimum exhaust NO was achieved with no reburning.

Data from Figures 3 and 4 are replotted in Figures 6a and 6b, respectively, to show the effect of SR_R on the various components of NO_x reduction by reburning. Overall NO_x reduction via reburning occurs by both the destruction of moles of NO produced in the primary zone and the "dilution" of the high NO primary zone gases by the staged fuel and air. The "dilution" portion of the overall NO reduction is calculated from the percent reburn load (assuming zero NO contribution by secondary combustion) and plotted as dashed lines on Figures 6a and 6b. In the case of distillate fuel oil, which contains virtually no fuel-bound nitrogen, the difference between the overall NO reduction curve and the dilution line represents the net destruction. In the case of the distillate/residual fuel oil mixture, the conversion of fuel nitrogen to N_2 is included in the net destruction component of overall NO reduction.

It has been shown in bench-scale tests (6), and verified in natural gas reburning tests in the PBS (15), that NO destruction is maximized for SR_R of about 0.9. This was found to be true of fuel oil reburning as well. This optimum is consistent with the minimum in the total fixed nitrogen (TFN) species equilibrium curve at the reburn zone temperature, though the experimental NO levels greatly exceed the equilibrium values under fuel-rich conditions. Thus, equilibrium is the driving force behind the reburning NO destruction kinetics.

Tests were conducted to compare fuel oil reburning effectiveness with natural gas reburning effectiveness. In these tests reburn zone bulk residence time was varied from 100 to 400 msec by varying the location of final air addition; the results are plotted in Figure 7. At the nominal reburn zone length of 0.61 m (24 in.), natural gas reburning was slightly more effective than distillate fuel oil reburning and much more effective than distillate/residual fuel oil reburning. It was originally hypothesized that low nitrogen fuel oil reburning would be more effective than actual gas reburning due to the higher carbon-to-hydrogen ratio in fuel oils that would produce more methyldine radicals than would be produced in methane combustion. Figure 7 shows that, for high reburn zone length residence times, distillate fuel oil reburning is slightly more effective than natural gas reburning at reducing NO. Fuel oil reburning requires longer reburn zone lengths to allow for vaporization of the droplets prior to ignition. For natural gas reburning, with the staged fuel injected circumferentially into the primary zone effluent to produce a uniform reburn zone stoichiometry, a fuel-rich zone length of 0.76 m (30 in.) was required to achieve maximum NO_x reduction. With a peak gas velocity in the reburn zone of 15 m/sec (50 ft/sec), as shown in Figure 2, this suggests a characteristic time of 50 msec for gas phase reburning reactions to occur. For the distillate fuel oil, approximately 1.0 m (40 in.) reburn zone length was required to maximize NO_x reduction. For the heavy fuel oil mixture, about 1.2 m (48 in.) reburn zone length was required. Photographs of the reburning fuel oil spray confirm that the fuel oil droplets persist several inches into the reburning zone.

Before discussing in-flame measurements of nitrogenous species, a parameter that was investigated and found to have little impact on the reburning NO_x reductions is mentioned. The fuel oil nozzle spray angle was varied from 30 to 90 degrees. In addition, various size nozzles were tested under identical conditions to investigate atomization effects. All of these nozzle variation tests yielded negligible effect on reburning effectiveness. Detailed measurements revealed that large scale turbulent structures existed in the reburning zone. Apparently, the combustion gas turbulent intensity dominated reburn zone mixing rates, resulting in NO_x emissions independent of oil injection methods. This result, which simplifies application, may be specific to the firetube package boiler class.

In-Flame Measurement Tests

Detailed in-flame sampling was performed for a variety of fuel oil reburning test conditions. NO, HCN, and NH_3 profiles in the reburn zone were measured, and total fixed nitrogen was determined by summing the three measured nitrogen species. Axial combustion gas profiles were obtained at a 13.3 cm (5.25 in.) radius. The species concentrations are ratioed to the primary NO corrected downward slightly to reburn zone molar concentrations. These profiles were not time resolved as large radial gradients in stoichiometry were observed, as well as large scale turbulent eddy structures. Thus, these trends are not representative of the entire boiler volume, but are useful in comparing different reburning conditions.

In Figure 8 reburn zone profiles for distillate fuel oil reburning at a 0.89 stoichiometry were measured for 200 and 80 ppm NO_{PRI}. The curves show that reburn zone reactions are delayed until about the 0.2 m (8 in.) axial location. Natural gas reburning, on the other hand, resulted in immediate nitrogen species reactions. The curves also indicate that there is no reduction in total fixed nitrogen (TFN) in the reburn zone for either test condition. In fact, for the 80 ppm NO_{PRI} condition, significant N_2 reduction occurred. It is hypothesized that this occurs

via Fenimore's prompt NO mechanism (N_2 reaction with methyldine to form HCN), since the temperatures in the reburn zone are well below the temperature necessary for Zeldovich reactions.

The difference between the TFN and NO curves represents the sum of the measured HCN and NH_3 concentrations. In all cases, NH_3 concentrations were less than 20 ppm. The low temperatures resulted in slow kinetics and no N_2 formation in the reburn zone. N_2 formation occurred in the burnout zone when the final air addition completed burnout of the hydrogen and carbon. In the reburn zone, the composition of the TFN was changed by the reaction:

$$NO + CH \longrightarrow HCN + O. \qquad (5)$$

The test conditions shown in Figure 8 and other test conditions indicate that this reaction is limited by the presence of CH radicals and not NO_{PRI}. That is, the reburn zone NO curve is a function of SR_R but not of NO_{PRI}. However, the TFN curve does depend on NO_{PRI}. The net moles of N_2 destruction (by the Fenimore mechanism and reburning fuel nitrogen) in the reburn zone appears to be a relatively constant 20 ppm. Thus, at lower NO_{PRI} this becomes increasingly significant, and overall NO reduction is reduced.

In Figure 9 reburn zone nitrogen species profiles are compared for two distillate fuel oil reburn loads: SR_R's of 0.89 and 1.03. Here it is shown that the reaction expressed by equation 5 is dependent on SR_R, with more NO being converted to HCN for more fuel-rich stoichiometries. Though the TFN is actually a greater percentage of the NO_{PRI} in the 0.89 SR_R condition, the composition of TFN is such that more N_2 formation occurs in the burnout zone, probably by the following reaction sequence:

$$HCN \xrightarrow{OH,H} NH \xrightarrow{NO} N_2. \qquad (6)$$

In the 1.03 SR_R reburn condition, little HCN is formed in the reburn zone so little N_2 formation occurs. The only reduction of NO_{PRI} that is achieved under this condition is via dilution of the primary flue gases by the low NO_x reburning flame gases.

Thus, in-flame measurements of intermediate nitrogen species confirm bench-scale experiments that suggest reburning mechanism. The qualitative argument presented here is based on typical data trends; however, the boiler volume is too large, and turbulent mixing too great, to provide a more quantitative analysis of the process.

Optimization Tests

The North American boiler was used to show how fuel oil reburning might be optimized in actual application. Baseline tests were performed to demonstrate that the North American boiler and PBS had similar thermal and aerodynamic environments in the radiant section. Reburning characterization tests were then performed to verify PBS test results. Finally, two optimized examples were performed and are presented here: distillate fuel oil reburning of a distillate fuel oil primary flame, and distillate/residual fuel oil reburning of a distil-

late/residual fuel oil flame. Constraints on these applications were to achieve good fuel burnout by minimizing fuel-rich zones and to compare conditions at full load, defined to be 650 kW (2.2×10^6 Btu/hr), and 15 percent excess air. These applications are shown in Figures 10 and 11 in a stepwise fashion to demonstrate how the overall NO_x reduction via reburning is achieved.

Initial NO levels of 125 ppm (dry, at zero percent O_2) and 265 ppm were observed for distillate and distillate/residual fuel oil firing, respectively. Step 1 consists of reducing primary flame excess air from 15 to 5 percent at full load. This resulted in reduced NO emissions of 21 percent for distillate oil firing and 26 percent for distillate/residual fuel oil firing. In step 2 the primary burner load is dropped by 20 percent, maintaining constant excess air. Some reduction in NO was achieved here due to the reduced mixing intensities in the primary flame. In step 3 reburning is applied, bringing the boiler back to a full load condition. Here, primary NO is reduced by staged hydrocarbon injection. Finally, the overall excess is increased to 15 percent resulting in slightly increased NO emissions. It is significant to note that the effect of increasing excess air in the burnout zone is less severe than the effect of decreasing excess air in the primary zone, due to lower flame temperatures in the staged combustion.

The overall NO_x reduction for the distillate fuel oil example was 46 percent; the overall NO_x reduction for the distillate/residual fuel oil example was 51 percent. Thus, approximately 50 percent NO_x reduction can be achieved via fuel oil reburning in the firetube package boiler.

CONCLUSIONS

The results from the firetube package boiler fuel oil reburning application tests demonstrate that 50 percent NO_x reduction is achievable with minimal retrofit modification requirement. The parametric tests indicate that, as primary NO_x is decreased, such as by low NO_x burner design, NO_x destruction via reburning becomes increasingly difficult, perhaps requiring the use of low nitrogen reburning fuels. There exists an optimum fuel-rich stoichiometry for reburning application of 0.7 to 1.0, dependent on system and fuel parameters. Distillate fuel oil reburning was shown to be slightly more effective than natural gas in reducing NO_x. However, fuel oil reburning requires longer reburn zone residence times than natural gas reburning due to droplet evaporation and mixing requirements. A minimum gas phase residence time of 50 msec is required to complete reducing zone reactions. In the firetube package boiler employed in this study, in which the peak combustion gas velocity in the boiler radiant section was 15 m/sec, a reburn zone residence length of 1.0 m or greater was required to optimize fuel oil reburning.

In-flame measurements of intermediate nitrogen species were consistent with proposed reburning NO reduction mechanisms. In the low temperature environment of this application (1300-1600 K), actual N_2 formation occurred in the burnout zone; in the reburn zone, total fixed nitrogen speciation was shifted from all NO_x in the primary zone to NO, HCN, and NH_3. Unpublished test results indicate that, although higher temperature fuel oil reburning applications result in increased reburn zone N_2 formation, higher temperatures in the burnout zone result in less N_2 formation. Thus, the net effect of temperature on the overall reburning process is not as dramatic as was first expected.

In optimizing reburning application to a firetube package boiler, while maintaining fuel-lean conditions in the primary zone to avoid boiler wall corrosion and/or sooting, reductions of about 50 percent were achieved for 20 percent

distillate and distillate/residual fuel oil reburning. The overall NO_x emission for distillate fuel oil firing was reduced from 125 to 68 ppm (dry, at zero percent O_2); for distillate/residual fuel oil firing the overall NO_x emission was reduced from 265 to 131 ppm (dry, at zero percent O_2).

ACKNOWLEDGMENT

This work was funded by EPA's Air and Energy Engineering Research Laboratory at Research Triangle Park, North Carolina. The authors wish to express their appreciation for the support provided by E. E. Stephenson and C. Pendergraph of Acurex Corporation.

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Table 1

FUEL ANALYSIS COMPARISON

Natural Gas	Distillate Oil	Distillate/Residual Oil Mixture
Gross Heating Value		
23,563 Btu/lb_f	19,382	18,734
15,225 W/(kg_f/hr)	12,523	12,105
Theoretical Air		
7.04 lb_a/10,000 Btu	7.48	7.58
10.90 (kg_a/hr)/W	11.58	11.73

Encal Chromatograph Analysis, mol. %:		Ultimate Analysis, wt %:		
Nitrogen	0.35563	Carbon:	6.44	87.12
Carbon dioxide	0.91649	Hydrogen:	13.21	11.97
Methane	96.11870	Nitrogen:	0.01	0.14
Ethane	1.85666	Sulfur:	0.22	0.84
Propane +	0.75252	Ash:	<0.01	0.02
		Viscosity, cs (ft^2/sec):		
		@ 38°C (100°F)	2.58 (0.0000278)	26.76 (0.0002880)
		@ 99°C (210°F)	1.08 (0.0000116)	4.68 (0.0000504)

Table 2

GASEOUS EMISSION MONITOR SPECIFICATIONS

Gas	Sample Type	Instrument Type	Manufacturer/ Model	Range
O_2	Continuous	Paramagnetic	Beckman/F3	0 to 5 10, 25%
CO_2	Continuous	Infrared	Beckman/864	0 to 5 10, 20%
CO	Continuous	Infrared	Beckman/865	0 to 500, 1000, 2000 ppm
NO_x	Continuous	Chemiluminescence	Teco/10A	0 to 2.5, 10, 25, 100, 250, 1000, 2500, 10000 ppm
THC	Continuous	Flame Ionization	Beckman/400	0 to 10, 100, 1000, 10000 ppm
NH_3	Batch-wet	Specific Ion Electrode	Orion/95-10	0.1 to 100 ppm
HCN	Batch-wet	Specific Ion Electrode	Orion/94-06	0.1 to 100 ppm
N_2O	Batch	Gas Chromatograph	Varian/1400	1 to 1000 ppm

TABLE 3

REBURNING PROCESS PARAMETERS

Primary Zone	Reburning Zone	Burnout Zone
° Initial NO_x Concentration	° Stoichiometry	° Stoichiometry
° Stoichiometry	° Residence Time	° Temperature
° Primary Fuel Properties	° Temperature	° Burnout Air Mixing Rate
	° Reburning Fuel Mixing Rate	
	° Reburning Fuel Properties (e.g., nitrogen content, volatility, C/H ratio)	

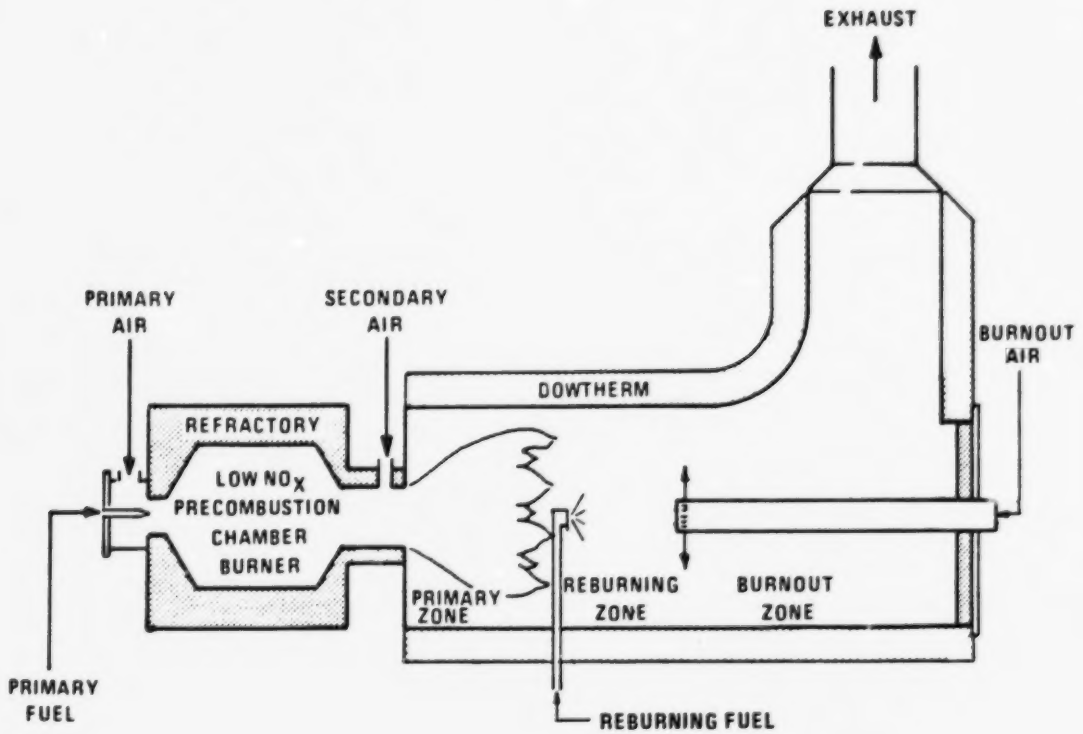

Figure 1a. Pilot-scale package boiler simulator test facility showing fuel oil reburning application.

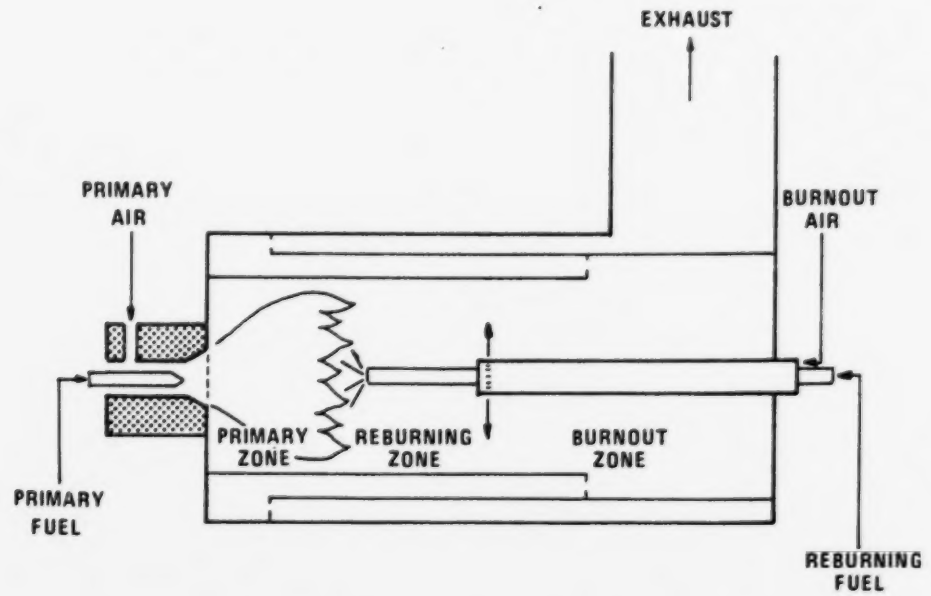

Figure 1b. Pilot-scale North American firetube package boiler showing fuel oil reburning application.

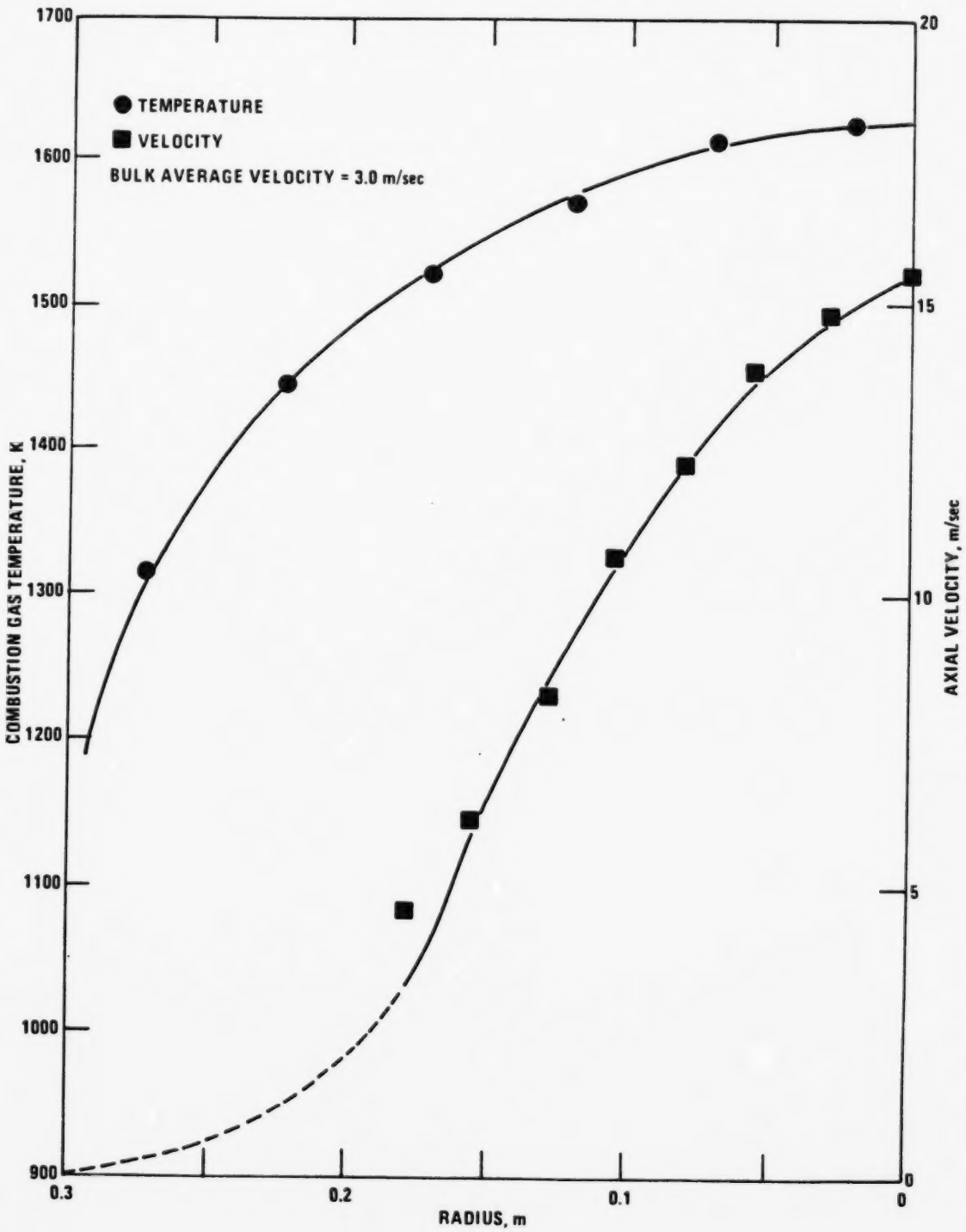

Figure 2. Baseline radial temperature and velocity profiles measured at the secondary fuel addition location.

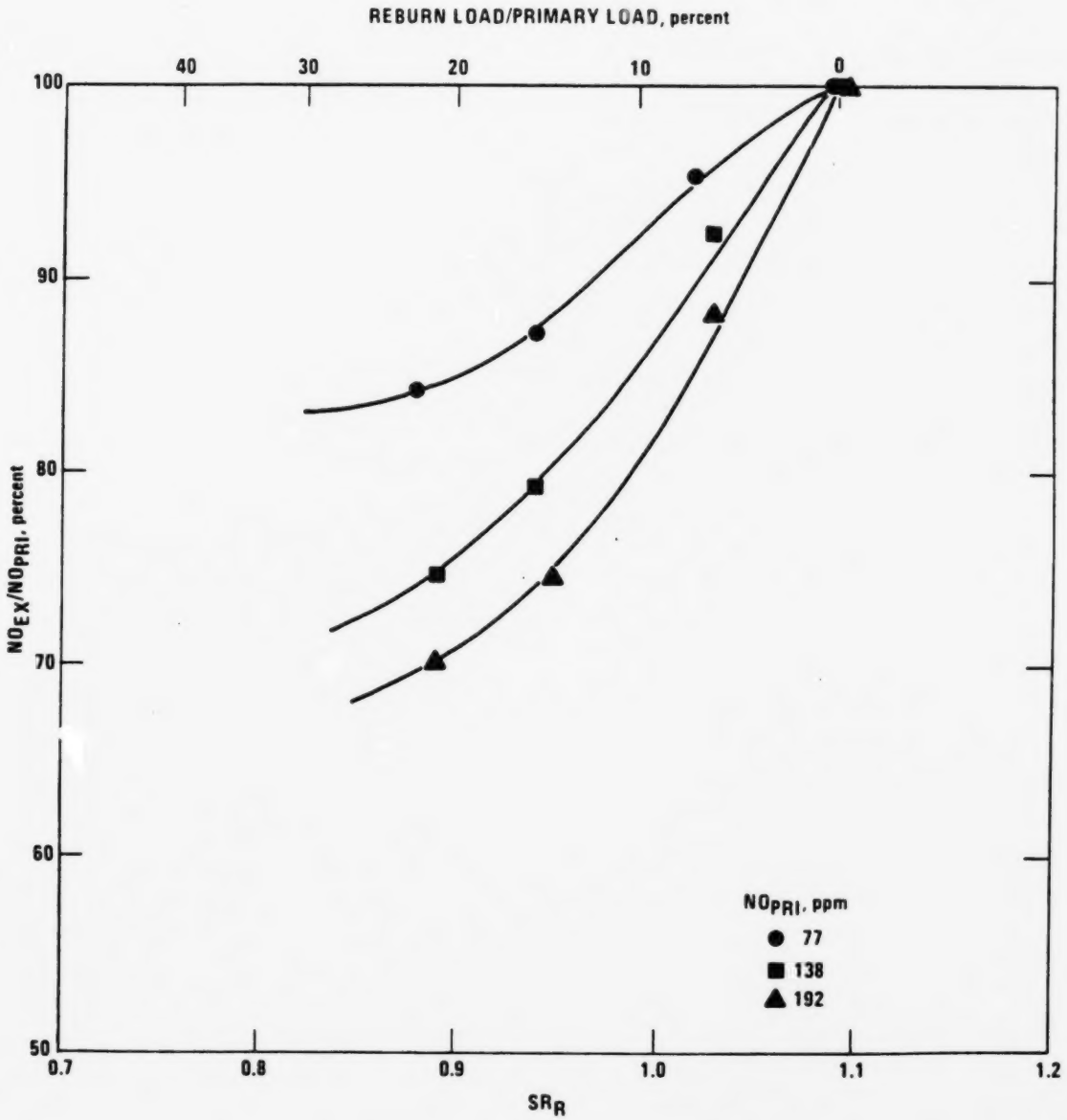

Figure 3. Exhaust NO as a function of reburn load for distillate fuel oil reburning.

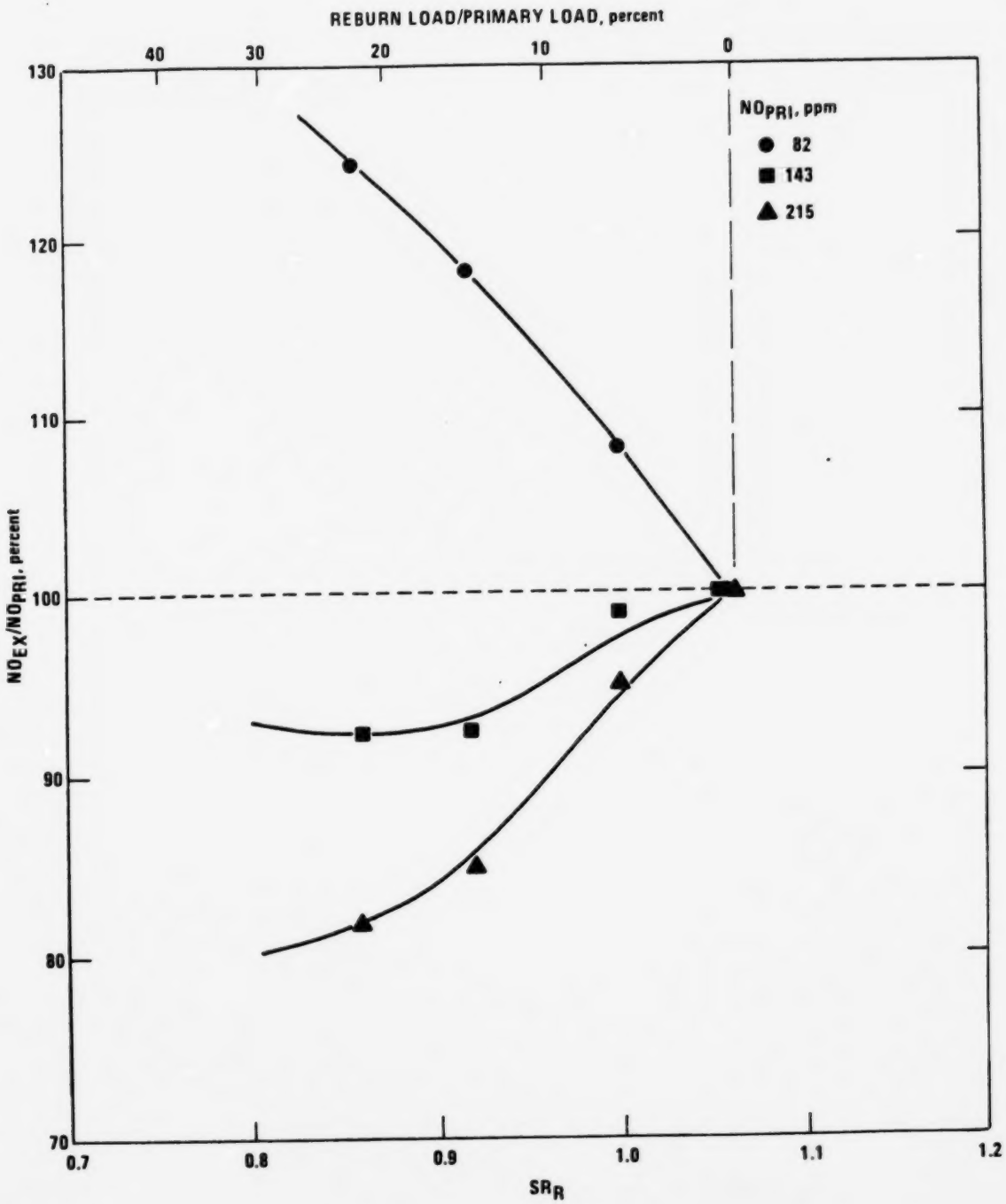

Figure 4. Exhaust NO as a function of reburn load for distillate/residual fuel oil mixture reburning.

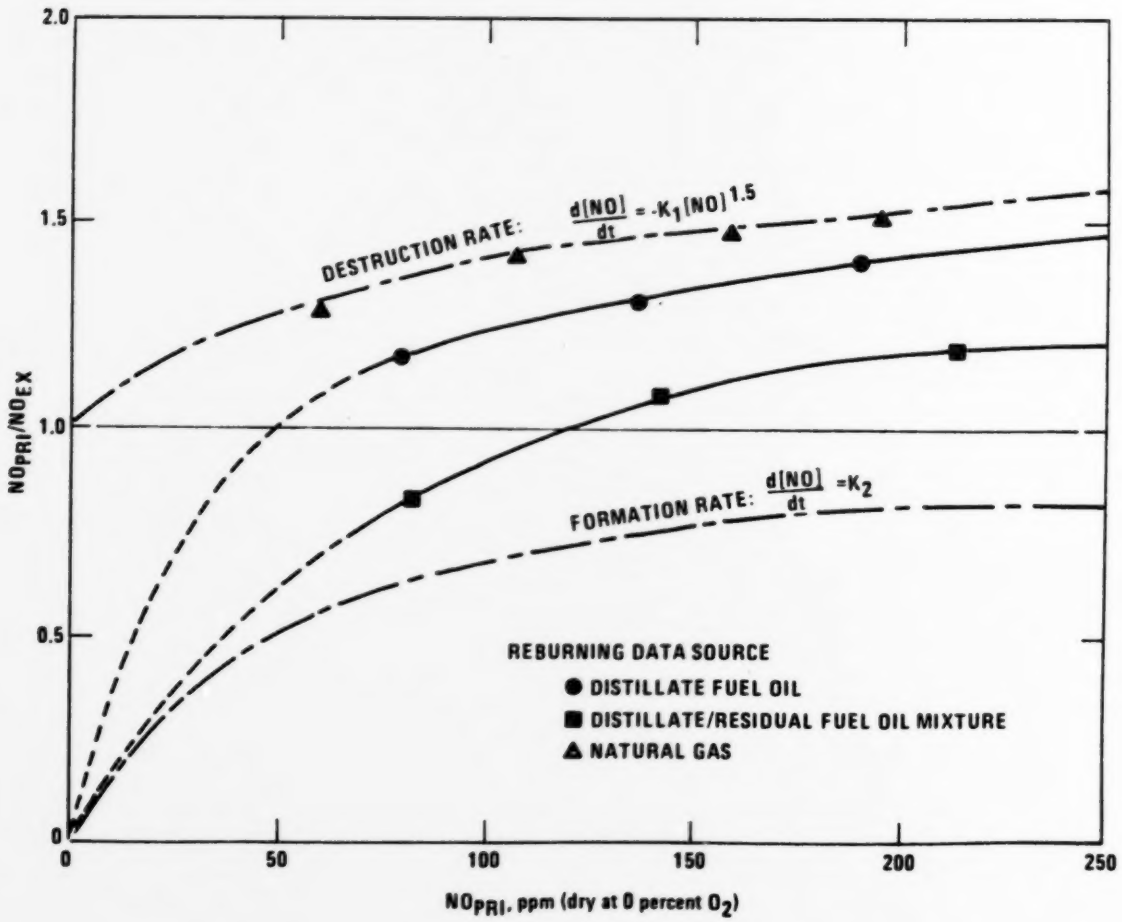

Figure 5. Exhaust NO as a function of primary NO for a reburn load of 20 percent of primary load.

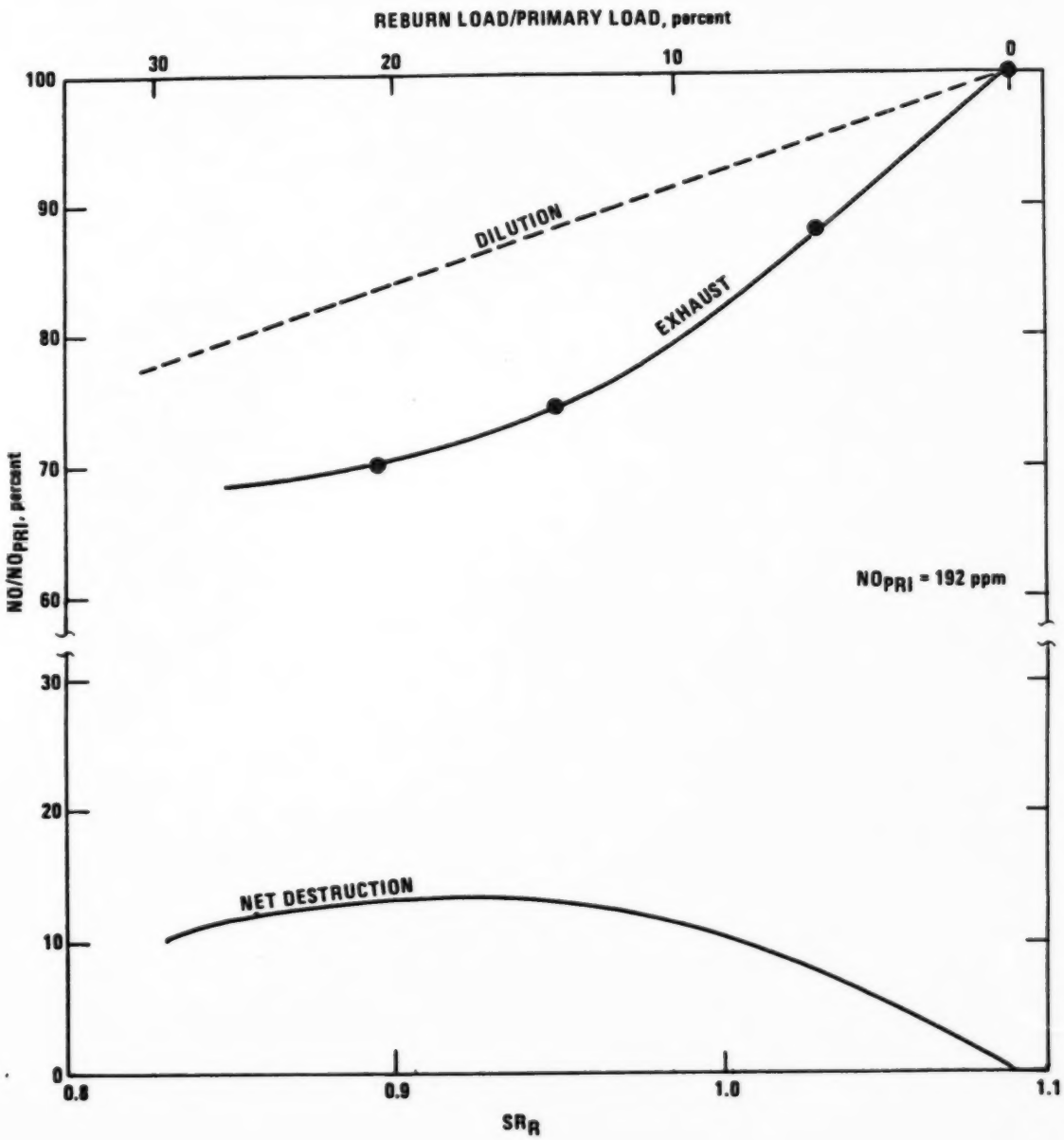

Figure 6a. Optimum stoichiometry for distillate fuel oil reburning.

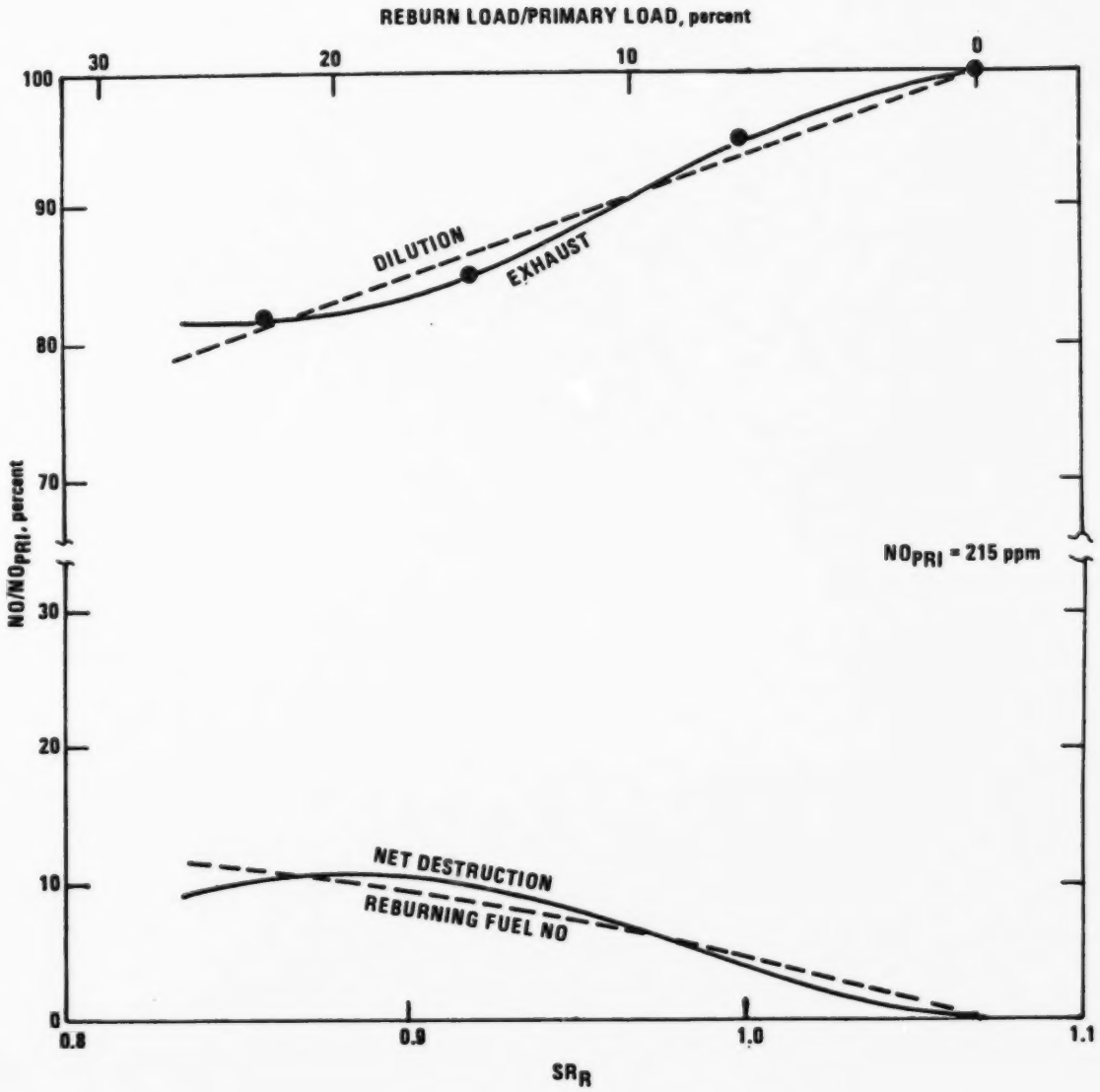

Figure 6b. Optimum stoichiometry for distillate/residual fuel oil mixture reburning.

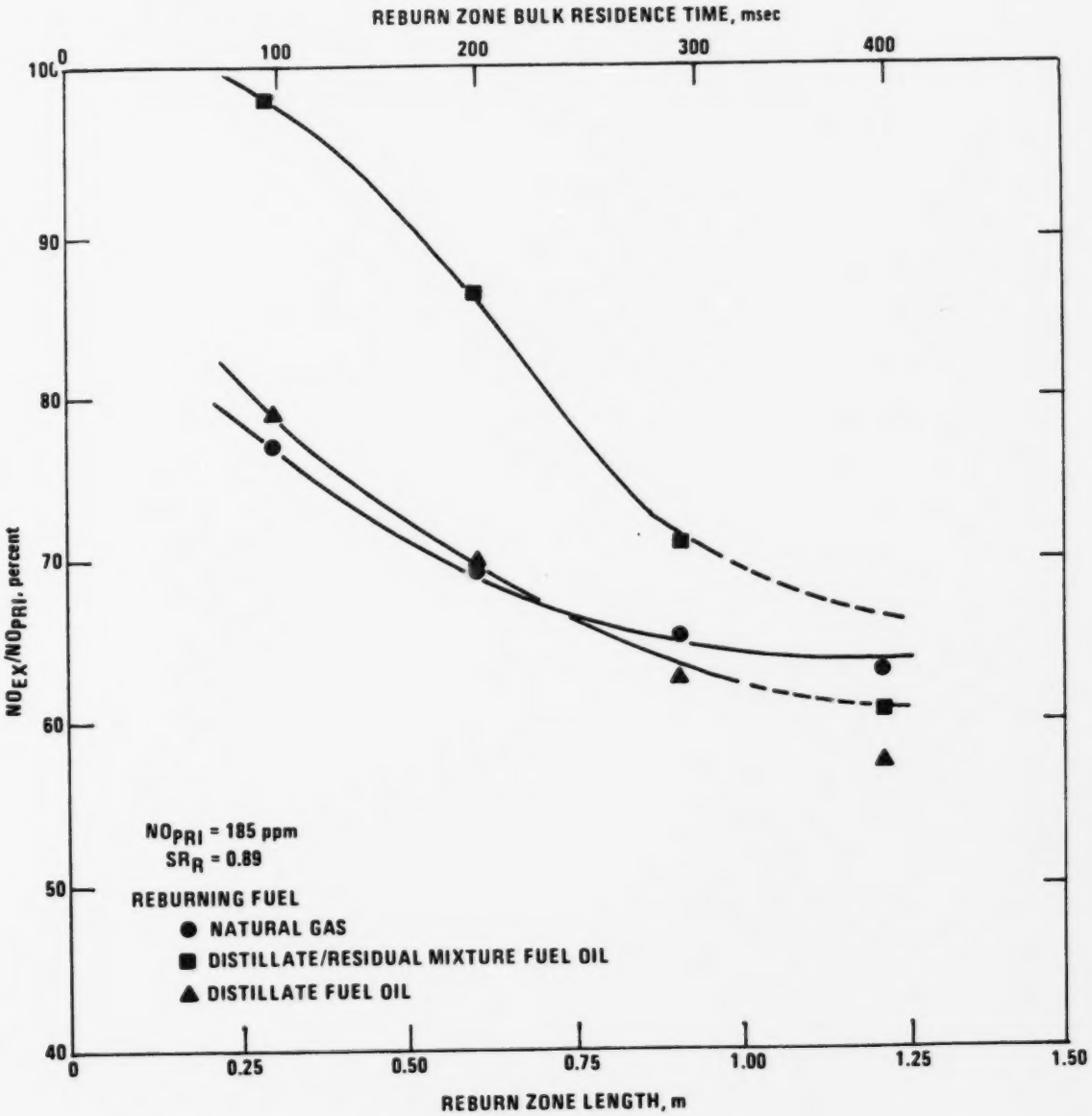

Figure 7. Exhaust NO as a function of reburn zone residence time.

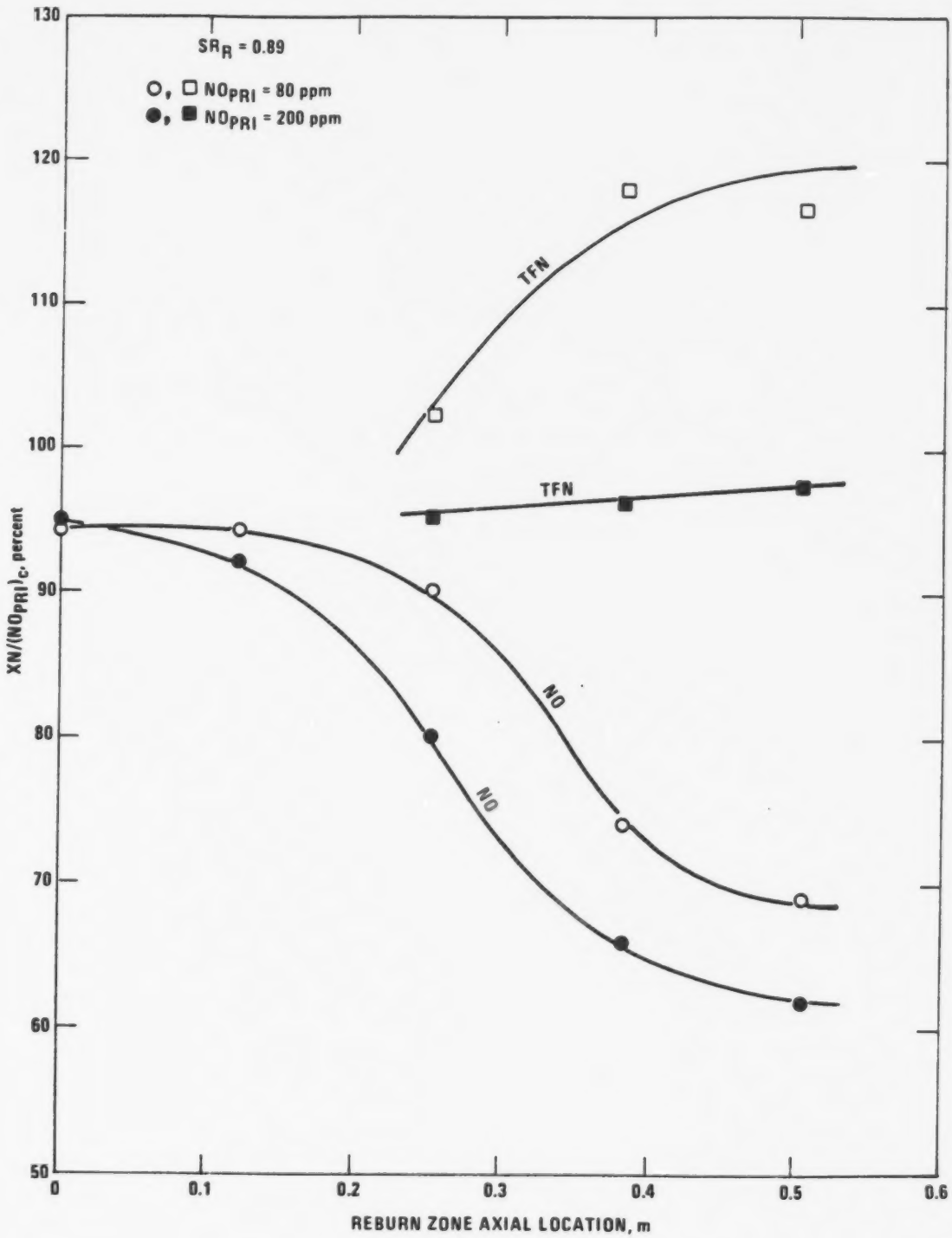

Figure 8. Reburn zone nitrogenous species profiles for distillate fuel oil reburning at NO_{PRI}'s of 200 and 80 ppm.

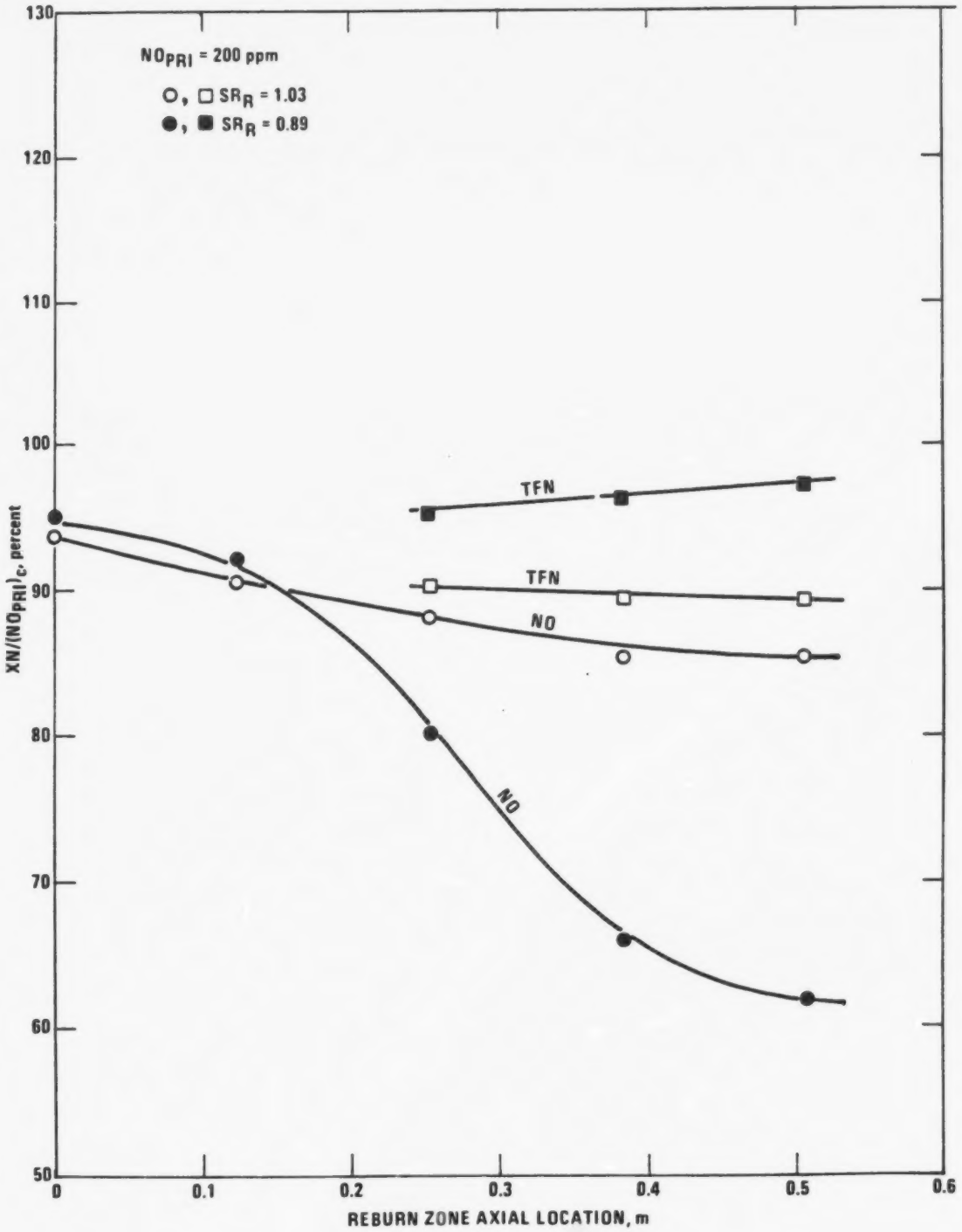

Figure 9. Reburn zone nitrogenous species profiles for distillate fuel oil reburning at SR_R's of 0.89 and 1.03.

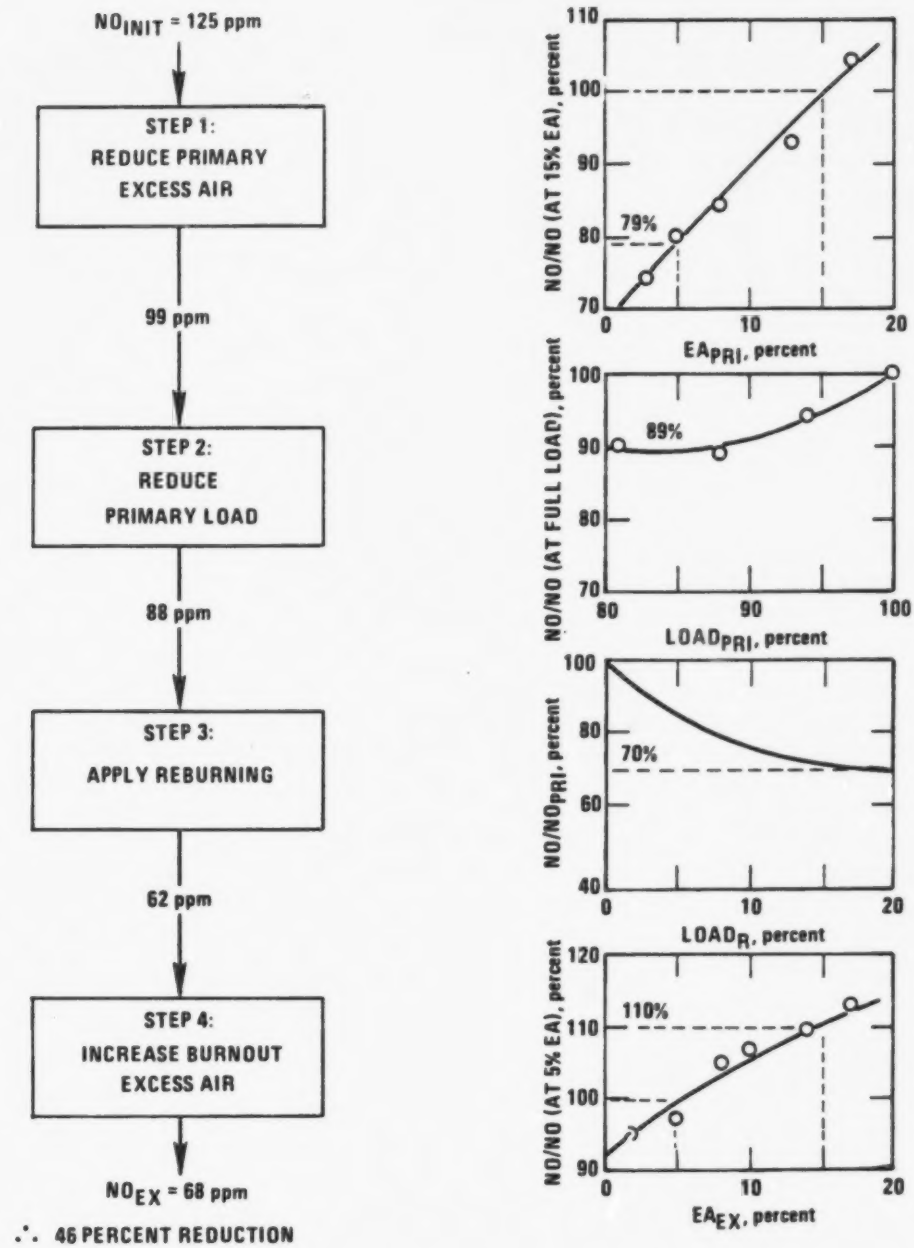

Figure 10. Distillate fuel oil reburning applications.

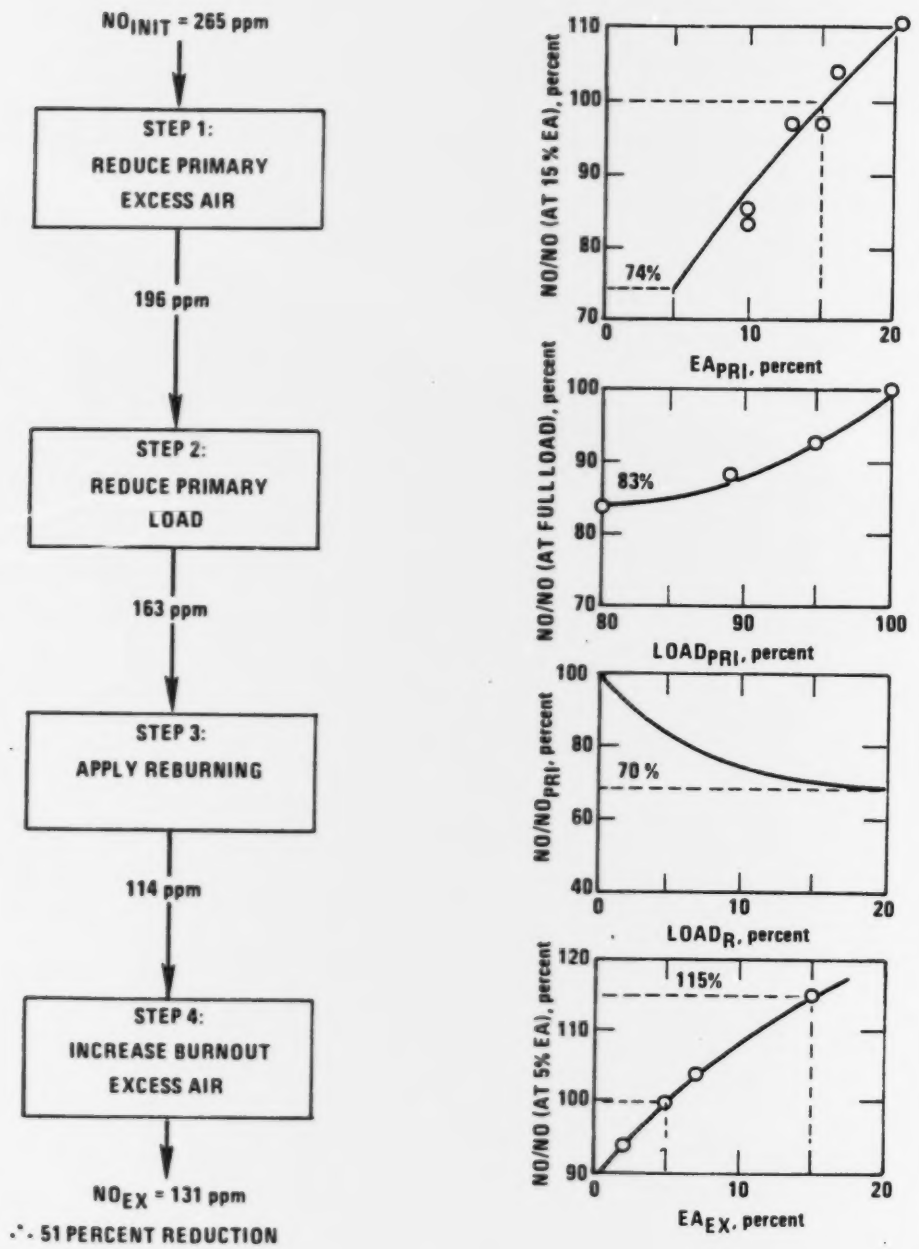

Figure 11. Distillate/residual fuel oil mixture reburning application.